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Fabrication of Highly *b*-Oriented MFI Film with Molecular Sieving Properties by Controlled In-Plane Secondary Growth

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Zeolites are crystalline materials with highly regular subnanometer-sized channels and a tunable composition. Zeolite powders are widely used as catalysts, ion exchangers, and adsorbents,[1] and zeolite films have great potential as separation membranes,[2−4] selective sensors,[5] optical materials,[6] and low-*k* materials.[7] In many cases, highly oriented zeolite films exhibit superior performance compared to randomly oriented ones,[8] which has aroused widespread interest. Among all the zeolites, the preparation of highly *b*-oriented MFI films is especially fascinating. Using direct in situ growth, Wang and Yan synthesized dense and highly *b*-oriented MFI films on smooth stainless steel substrates by accurately manipulating the experimental conditions and precursor compositions.[9] Highly *b*-oriented and twin-free MFI membranes were also prepared by secondary growth of an MFI seed layer in Tsapatsis' group, using the specifically designed trimer-TPAOH as a structure-directing agent (SDA) to drive *b*-oriented growth.[2] Much higher permeance and selectivity were then obtained for the separation of *o*-/*p*-xylene vapors than on other MFI membranes.

Secondary growth is better suited for the fabrication of oriented MFI films as the film quality is less affected by substrate conditions, and the reproducibility is relatively high.[10] However further innovations are urgently required for scalable applications. For instance, it will be beneficial if a facile and efficient method is developed to organize MFI seed crystals on substrates with unfavorable surface conditions, and commercially available organics is used as the SDA instead of trimer-TPAOH.

To seek a preliminary solution to these problems, here we developed a new route for the synthesis of highly *b*-oriented MFI films. First, relatively large MFI microcrystals (∼1.6 μm) of well-developed shapes were selected as seeds to reduce the density of grain boundaries[2] and, thus, the grain boundary diffusion resistance.[11] Second, a novel interface-aided seeding method was applied to orient these large crystals on substrates.[12] Finally, TPAOH was used as the SDA during the secondary growth. It is generally believed that twin growth is unavoidable with template TPAOH, which negatively affects the quality of the as-prepared zeolite films.[2] Unexpectedly, we found that proper optimization of the secondary growth process resulted in predomination of in-plane over twin growth, thus preserving the crystallographic orientation of the zeolite seed crystals. To the best of our knowledge, this is the first report confirming that twin growth of a *b*-oriented MFI seed layer can be effectively suppressed with TPAOH as the template during secondary growth.

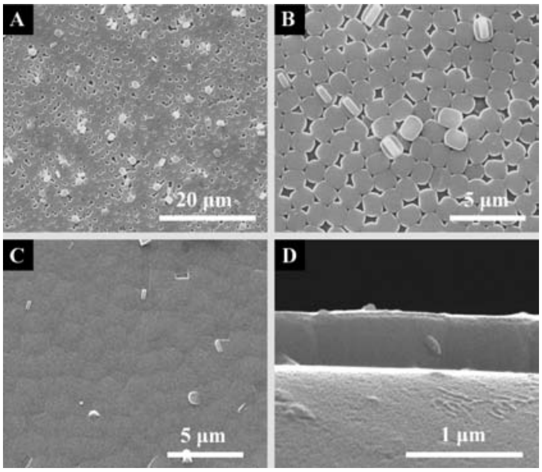

Figure 1. SEM images of (A, B) as-prepared MFI seed layer, (C) as-prepared MFI film after secondary growth on glass plate, and its (D) Cross-sectional image.

A *b*-oriented MFI seed layer was prepared as follows. Briefly, a certain amount of DDI water was dropped onto a precleaned substrate to serve as a temporary soft substrate. Then an as-prepared zeolite suspension (MFI microcrystals evenly dispersed in *sec*-butanol and trace amount of linoleic acid (LA)) was slowly injected onto the air−water interface until a continuous monolayer formed. Controlled evaporation of the liquid layer yielded a compact and highly *b*-oriented MFI monolayer on the substrate, and the SDA was finally removed by calcination.

In the next step, a freshly prepared clear precursor solution was hydrothermally pretreated in an autoclave. The seeded substrate was then immersed in this solution, and secondary growth was allowed to proceed. After washing and drying, the sample was calcined to remove template occluded in MFI micropores. Further details can be found in the Supporting Information.

With SEM characterization, it was observed that the MFI seed layer was compact and uniform (Figure 1A and 1B), with nearly every zeolite microcrystal anchored to the glass substrate by its largest facet and closely contacted with each other. Compared with the first layer, only 2.90% MFI microcrystals were sparsely deposited in the second layer (Figure 1A). XRD characterization confirmed strong *b*-orientation, and [0*k*0] reflections dominated in the diffraction pattern, as shown in Figure 2B. Here we propose that hydrophobic interaction between LA molecules adsorbed on different zeolite microcrystals may reinforce their attractive interaction, thus forming more compact zeolite monolayers in a mechanism similar to nanoparticle self-assembly on a nanometer scale.[13] We believe that other regular microparticles could also be assembled into densely packed monolayers with this method.

After secondary growth, a continuous and crack-free MFI film formed (Figure 1C), and zeolite seeds had grown bigger and merged with each other very well. Meanwhile, the as-prepared zeolite film was still dominantly *b*-oriented with rare twin growth (Figure 2C, a higher magnification was listed in Figure S1). Moreover, the SEM

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10.1021/ja909888v

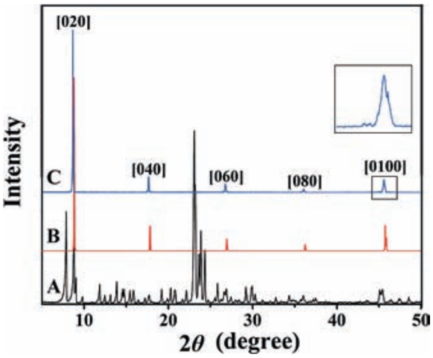

Figure 2. XRD patterns of (A) MFI powder, (B) as-prepared MFI seed layer, and (C) as-prepared MFI film after secondary growth on glass plate. Inset: Enlarged image of peak [0 10 0].

cross-sectional view from Figure 1D illustrated that the film was 630 nm thick, with only a 3.2% increase in size along the *b*-axis compared to the seed crystals (Figure S2), implying that undesirable twin growth of the MFI seed layer had been effectively inhibited.

Without hydrothermal pretreatment of the precursor, substantial twin growth was observed in our system (Figures S3 and S4). The large discrepancy between the treated and untreated precursor solution can be interpreted as follows. Without preheating, the precursor concentration was too high, thus favoring new nucleation and the subsequent twin growth on the seed layer. With preheating, however, zeolite nucleation had been accomplished in the precursor solution, leaving only in-plane growth of the seed layer during the subsequent secondary growth. More in-depth discussion can be found in the Supporting Information (Figure S5). Very recently, this precursor pretreatment method was also used to try directing the *c*-oriented growth of $AlPO_4$-5 films.[14] These results unambiguously demonstrate that the growing dynamics of zeolite seed layers can be well manipulated by process optimization.

Besides glass plates, quartz plates, stainless steel plates, mixed oxides disks, and platinum electrodes were also used as substrates to grow MFI films. As shown in Figure S6, high quality zeolite films were grown on all of these substrates, regardless of their surface conditions, proving the generality of this method.

We further verified the molecular sieving properties of the *b*-oriented MFI layer by fabricating it onto a Pt electrode (Figure S6L). This zeolite-modified electrode (ZME) was then used as a working electrode in the following electrochemical experiments. Redox species of varying charge and size in aqueous solution, including $[Fe(C_5H_5)_2]^+$ (diameter ~5.5 Å), $[Fe(CN)_6]^{3-}$ (diameter ~7.2 Å), and $[Fe(phen)_3]^{2+}$ (diameter ~13.0 Å), were tested. The pore size of the MFI crystals along the *b*-axis is 5.5 Å, so we expected that $[Fe(C_5H_5)_2]^+$ was able to pass through the MFI layer and undergo redox reactions on the Pt electrode but that $[Fe(CN)_6]^{3-}$ and $[Fe(phen)_3]^{2+}$ would be excluded. Cyclic voltammetry (CV) experiments were carried out to investigate its redox properties.

Figure 3 showed the CV curves for different ionic species. Compared to a bare Pt electrode, a weaker and deformed CV signal was detected for $[Fe(C_5H_5)_2]^+$ on the modified electrode (Figure 3A), while no CV responses were found for $[Fe(CN)_6]^{3-}$ (Figure 3B) and $[Fe(phen)_3]^{2+}$ (Figure 3C). For a mixture of $[Fe(C_5H_5)_2]^+$ and $[Fe(phen)_3]^{2+}$, only the redox signal for $[Fe(C_5H_5)_2]^+$ was detected (Figure 3D). All these results strongly proved the molecular sieving ability of the *b*-oriented MFI layer.

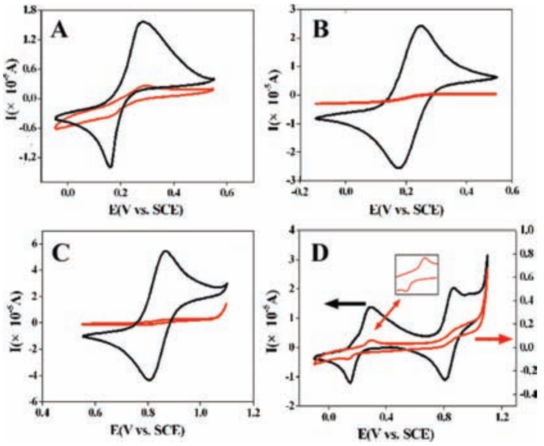

Figure 3. Cyclic voltammograms of $[Fe(C_5H_5)_2]^+$, $[Fe(CN)_6]^{3-}$, and/or $[Fe(phen)_3]^{2+}$ in aqueous solutions. Black line: bare Pt electrode; red line: Pt electrode coated with *b*-oriented MFI films for (A) $[Fe(C_5H_5)_2]^+$, (B) $[Fe(CN)_6]^{3-}$, (C) $[Fe(phen)_3]^{2+}$, and (D) $[Fe(C_5H_5)_2]^+ + [Fe(phen)_3]^{2+}$. Supporting electrolyte: 0.5 M KCl. Scan rate: 50 mV/s. Reference electrode: sodium saturated calomel electrode (SCE).

In summary, here we developed a simple and economic route for growing highly *b*-oriented and submicrometer thin MFI films on various substrates. The MFI layer showed a size-selective molecular sieving ability as a zeolite-modified Pt electrode. In future work we will further optimize the microstructure of this *b*-oriented MFI film and explore its potential use in various fields.

Acknowledgment. This work was supported by the National Science Fund for Distinguished Young Scholars (20725313), the DICP Independent Research Project (No. R200807), and the Ministry of Science and Technology of China (Grant No. 2003CB615802). We sincerely thank Prof. Y. S. Yan from UC Riverside for his great help in electrochemical experiments.

Supporting Information Available: Experimental details and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA909888V